Florida Department of Agriculture & Consumer Services
CHARLES H. BRONSON, Commissioner

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May 8, 2008

Ms. Cynthia Giles-Parker
USEPA Registration Division
Ariel Rios Building
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1200 Pennsylvania Ave., NW
Washington, DC 20460–0001

Re: Ground water advisory statements and iodomethane

Dear Ms. Giles-Parker:

In Florida, the Department of Agriculture and Consumer Services (FDACS) serves as the state lead agency for registration and regulation of pesticides. Florida Statutes direct FDACS to seek review and comment from other state agencies as part of our pesticide registration process. Among our state agency partners, the Florida Department of Environmental Protection (FDEP) is noteworthy for its expertise in protecting the quality of Florida's water resources. Technical experts in FDACS and FDEP regularly share assessments of the potential impacts of pesticides on Florida ground and surface water and typically, we find ourselves in close agreement regarding pesticide regulatory decisions arising from these collaborative efforts.

In May 2007, FDEP brought to our attention inherent problems with a ground water advisory statement on the label of a fungicide, prothioconazole (Proline and Provost). The advisory stated:

> "Prothioconazole-desthio (a degradate of prothioconazole) is known to leach through soil into ground water under certain conditions as a result of label use. Use of this chemical in areas where soils are permeable, particularly where the water table is shallow, may result in ground water contamination."

Pesticides with such ground water advisories are not uncommon, but this was the first instance in which the statement came under close scrutiny during the Florida registration review process. Both of our agencies concluded that when used according to label instructions, this fungicide would not pose unacceptable risks to the ground water resource. Further, we agreed that the water quality advisory introduced a number of interpretative problems. Given FDEP's responsibility to protect ground water resources, they indicated an inclination to object to the registration of a product whose label indicates that the product could "contaminate" ground water when used in Florida. FDEP's Office of General Counsel also noted that the precautionary statement was vague, since the statement does not clarify what is meant by "permeable" soils or "shallow" water tables, conditions which could exist throughout the state. The advisory statement also does not provide instructions on what an applicator can do to avoid contamination. Moreover, the statement could transfer liability for ground water contamination from the registrant to the applicator. FDEP noted that, with all other things being equal, if a label lacks the advisory statement and proper use results in ground water contamination, then the state of Florida would hold the registrant liable for cleanup costs. However, if the statement were present, the liability for cleanup would shift to the applicator.

Prothioconazole ultimately was registered in Florida, however, FDACS and FDEP agreed that such water quality advisory statements created more confusion than clarity, and they lacked meaningful guidance for applicators. FDACS is committed to dialogue with other states and the U. S. Environmental Protection Agency (USEPA) to further explore problems involving water quality advisory statements. Our initial inquiries have led to additional questions, some of which have been raised at recent SFIREG Water Quality and Pesticide Disposal Committee meetings. For example:

1. With regard to interpretation of field dissipation data, the decision to include an advisory statement does not appear to be risk-based, but rather based on whether <u>any quantity</u> of pesticide, regardless of concentration, is detected below ground surface. In the case of prothioconazole, the choice of the advisory statement appears to have been based on the detection of toxicologically insignificant concentrations of a prothioconazole degradate between 12 and 18 inches below the surface;

2. There appears to be inconsistency at the Agency in the implementation of this policy on ground water advisory statements. For example, FDACS has identified product labels for which, based on the Label Review Manual, the active ingredient's chemical properties should warrant a statement on the label, yet no statement appears (e.g., Cobra Herbicide and Sapphire Herbicide). In other cases, the choice of the advisory statement is in question (e.g., Actara Insecticide).

The issue of ground water advisory statements recently has risen to a critical level in Florida. As FDACS nears the end of a lengthy and thorough evaluation of the application for Florida registration for the new soil fumigant, iodomethane, we have learned that the Agency is requiring a ground water advisory statement on the Section (3) product labels. This was unanticipated, since neither the Agency's nor Florida's risk assessment concluded that use of iodomethane posed a threat to ground water. The Agency apparently had inadvertently omitted the statement from the Section (3) label for all iodomethane products registered in 2007. Thus, the advisory did not appear on the label we originally reviewed nor does it appear on the labels of iodomethane products already registered in more than 40 states.

The required statement on the Midas labels is as follows:

> "Iodomethane has properties and characteristics associated with chemicals detected in ground water. The use of this chemical in areas where soils are permeable, particularly where the water table is shallow, may result in ground-water contamination."

It is our understanding that the Agency required this advisory statement since the K_d and hydrolysis values for iodomethane meet criteria established in the USEPA Label Review Manual.

Subsequently, the Agency added to the statement, as follows:

> "Iodomethane has properties and characteristics associated with chemicals detected in ground water. The use of this chemical in areas where soils are permeable, particularly where the water table is shallow, may result in ground-water contamination. Avoid slicing or removing the tarp if it is raining or if rain is expected within 48 hours. Rain may cause iodomethane remaining under the tarp to contaminate ground and/or surface water. This advisory does not include planting with the tarp in place."

In response, the registrant, Arysta Life Sciences, proposed an alternative statement to address conditions in Florida, as follows:

> "Iodomethane has properties and characteristics associated with chemicals detected in ground water. The use of this chemical in areas where soils are permeable, particularly where the water table is shallow, may result in ground-water contamination.
>
> For broadcast applications, avoid slicing or removing the tarp if it is raining or if rain is expected within 12 hours. For raised bed applications, rainfall is not a factor as planting occurs with the tarp in place; and slicing or removing of tarps occurs after iodomethane has dissipated."

FDACS is proposing that the Agency accept the following alternative:

> "Iodomethane has certain properties and characteristics associated with chemicals detected in ground water. However, its volatility and application under plastic film greatly diminish the potential for ground water contamination. Therefore, for broadcast applications, avoid slicing or removing the tarp if it is raining or if rain is expected within 12 hours. For raised bed applications, rainfall is not a factor as planting occurs with the tarp in place and slicing or removing of tarps occurs after iodomethane has dissipated."

Our reasons for requesting this revision of the advisory statement are as follows:

(1) The Agency's own risk assessment indicates that the ground water advisory is unnecessary. The Agency's analysis reported: "Iodomethane is very soluble in water, so there is the possibility of leaching to ground water and/or transporting to surface water through runoff, if slicing or removal of the tarpaulin coincides with, or is followed soon by, a rain event. Therefore, a qualitative drinking water assessment was performed for this risk assessment. Tier II PRZM/EXAMS for surface water and Tier I SCIGROW for ground water were used to estimate iodomethane concentrations in drinking water. Since

iodomethane is a volatile compound, additional input parameters like DAIR (vapor phase diffusion coefficient) and ENPY (enthalpy of vaporization) were activated during the PRZM-EXAMS simulation. In the absence of monitoring data, the concentration of iodomethane in ground water was estimated using SCIGROW, which has limited capability to perform vapor phase transport of iodomethane to ground water. The assessments were based on maximum application rate of iodomethane for pepper in Florida and generally represent upper-bound estimates of iodomethane concentrations that might be found in surface water and ground water. <u>Based on environmental fate data, the residual contents in soils, and Tier I and II models estimated concentrations, the Agency does not expect iodomethane to adversely impact ground water or surface water (emphasis added)</u>." The risk assessment concluded, "…<u>a qualitative drinking water risk assessment has been conducted and no risks have been identified from this potential source of exposure</u>."

If no risks have been identified, there should be no need to raise concern for ground water contamination on the label.

(2) Florida's risk assessment also leads us to believe that including the original ground water advisory is overly conservative. We conducted a comprehensive review (summary attached) including modeling of the fumigant's fate in soil and ground water under very conservative conditions and concluded that the pesticide does not pose an unacceptable risk to ground water quality. Iodomethane is a non-persistent, volatile soil fumigant that is applied beneath a tarp that is impervious to rain. Fumigant applications are also made pre-plant, to moist, not saturated, soil; by preventing the rain from percolating through treated soil and not irrigating following the application, there would be minimal water available to mobilize the pesticide to the water table. Moreover, applications are conducted under a tarp that remains in place for the entire growing season (raised bed) or is removed only after a minimum 5-day post-application period (10 days for highly retentive films). These practices will allow for loss of the product by volatilization and degradation and ameliorate the potential for movement to ground water.

(3) The introductory sentences in the original ground water advisory do not impart meaningful information. They do not take into account the mitigation provided by tarping and volatility, as mentioned above, and they do not instruct an applicator on what is meant by a highly permeable soil or a shallow water table. Since most of Florida has permeable soils and shallow water tables, what are growers here to do differently when applying the product?

(4) The advisory statement may, without good cause, shift liability for ground water clean up from the registrant to the applicator.

(5) The Agency's Label Review Manual (LRM) allows the Agency to exercise discretion in requiring ground water advisory statements. Chapter 8(II)(D)(4) of the LRM states:

Ground Water Advisories

If the environmental reviewers determine that the chemical (or major degradates) has laboratory-derived mobility (Kd less than 5) and persistence characteristics (e.g., hydrolysis half-life at any pH greater than 30 days or aerobic soil metabolism half-life greater than 2 weeks) similar to other pesticides found in ground water as a result of normal label uses, and no detections are reported in ground water (for example, for a new chemical), the Agency *has generally required* (emphasis added) the following label language:

Ground Water Advisory

"This chemical has properties and characteristics associated with chemicals detected in ground water. The use of this chemical in areas where soils are permeable, particularly where the water table is shallow, may result in ground-water contamination."

The USEPA's discretion regarding ground water advisories is further characterized in a response on the Agency's website for frequently asked questions about pesticide regulation, http://www.epa.gov/opp00001/regulating/labels/label_review_faq.htm. The questions and answer are as follows:

Question: Chapter 8. II. D. 4 of the Label Review Manual indicates when Ground Water Advisories are "generally" required. However many labels for outdoor use meeting the specified thresholds do not have such advisories. Imidacloprid meets the specified thresholds for the advisories and has been detected in ground water in Long Island, NY. The labeling for the agricultural product has the ground water advisory, but the label for the termiticide product does not. Why the inconsistency? LC08-0143; 1/10/08

Answer: As pointed out in the Chapter 8.II.D.4, Ground Water Advisories are "generally" required. *The ground water advisory is a case-by-case basis determination depending on the use site and available data* (emphasis added). Termiticides uses are generally considered indoor uses because applications involve injection through drilled holes in slabs of constructed houses, or for pre-construction, the soil is sprayed just before the foundation is poured. Under such circumstances, OPP has not generally required ground water advisories.

The iodomethane registration review has been a highly significant undertaking in Florida. Scientists in FDACS and in our sister agencies have committed great effort to reviewing the Federal risk assessment as well as the registrant's data and the open literature. Our review has resulted in the identification of a large number of deficiencies relating to clarity, enforceability, and risk mitigation in the Section 3 label. As we have addressed these concerns with the registrant, we have also coordinated closely with USEPA. We believe that our review has led to significant improvements in the product label, and that these improvements would be reflected in a stand-alone Florida supplemental label, assuming Florida will register iodomethane products.

While essentially all of our other labeling concerns have been addressed, the issue of the ground water advisory statement remains a major hurdle to a consensus decision for state registration. We believe that the current label statement is inappropriate; it adds to the uncertainty of the iodomethane registration in Florida, along with the yet unknown additional mitigation measures that may arise from the fumigation cluster assessments. Therefore, we would greatly appreciate the Agency's assistance in carefully reviewing the question of applicability of a ground water advisory statement on Section (3) labels for iodomethane products and/or for stand-alone supplemental labels for iodomethane products in Florida.

We intend to pursue a longer-term review of ground water advisory statements for other products through SFIREG and AAPCO and through the Florida Pesticide Review Council, which has established a committee to address the impacts of these advisory statements on pesticide registrations in Florida.

Thank you for your consideration. We look forward to continuing to work with you toward the resolution of this important issue.

Sincerely,

CHARLES H. BRONSON
COMMISSIONER OF AGRICULTURE

Dennis F. Howard

Dennis F. Howard, Ph.D.
Chief, Bureau of Pesticides

Cc: Mr. Anderson H. Rackley
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ENVIRONMENTAL FATE and TRANSPORT

Computer Model Simulations

GROUND WATER MODELING

SCI-GROW
(S)creening **(C)**oncentration **(I)**n **(Gro)**und **(W)**ater
Sci-Grow is a screening model for leaching of pesticides to shallow ground water. This model uses the soil metabolism, soil adsorption, and the amount of pesticide applied to estimate the long term concentration expected in ground water. The model is considered conservative in its estimates since it is based on studies conducted on sites with shallow water tables, sandy, highly permeable soils and high amounts of rainfall and irrigation to promote leaching. Sci-Grow is probably not conservative for the majority of Florida sites. The suitability of Sci-Grow for a fumigant is also doubtful since it has no volatilization component.

The EPA used the following iodomethane variables: aerobic soil half-life = 0.25 days, Koc = 35, one application of 175 lbs a.i./acre. The long-term ground water concentration is estimated to be less than 9 parts per trillion (pptr). When a 5 day half-life is used from the Florida terrestrial field dissipation study, the long-term ground water concentration is estimated to be 840 parts per trillion. The terrestrial field dissipation half-life is the summation of all pathways (biotic and abiotic) of degradation under field conditions.

PRZM 3.12
Tier II computer simulations were also attempted to better understand the potential for iodomethane to move to ground water. The PRZM 3.12 (Plant Root Zone Model) in the USEPA, Express Shell v 1.00.00.03. was used to simulate the movement of iodomethane in a tomato field in South Florida. The Florida-tomato scenario uses a Riviera fine sand with West Palm Beach weather data (1961-1990).

Since tomatoes can be grown at two times per year, FDACS completed simulations with either a January 31st or August 31st application. The application date was ten days before tomato seedlings were placed in the field to allow for degassing. Since the influence of the HDPE tarp on volatilization could not be directly simulated in the model, the terrestrial field dissipation half-life (5 days) was used. In the Florida terrestrial field dissipation study, the iodomethane was shank applied to beds covered with a plastic tarp. A first order regression of the iodomethane remaining in the top 1.22 meters of the soil over the 90 day study provided an R^2 of 0.99. The losses during this study were primarily due to volatilization. This half-life was used as the aerobic soil input for the upper one meter of the soil profile and to represent all losses of iodomethane (hydrolysis, soil metabolism and volatilization). All other PRZM inputs influencing hydrolysis and volatilization in the upper soil were set to zero. In the 0 to 10 cm and 10 to 100cm soil horizons, Kds of 0.4 and 0.04 mL/g were used.

The soil profile was extended to 500 cm (15 feet) so leaching out of the bottom of the soil profile could be simulated. Below the 100 cm depth, the Kd was set at 0.04 mL/g and a soil half-life of 150 days was used. This half-life represented the potential losses from hydrolysis.

Other inputs used were: CAM (chemical application method) = 8, with a 20 cm application depth, 175 lbs iodomethane, one application per year (January 31 or August 31), irrigation during growing season, molecular weight = 142.0, water solubility = 14,200 ppm, aerobic soil half-life = 5 days, no volatilization, hydrolysis = 0, EPA Florida tomato parameters.

As was intended by shutting off the volatilization inputs, no iodomethane was lost in runoff water or on eroding soil. In real life applications, the placement of the plastic tarp immediately after application will prevent most of the iodomethane losses to runoff water and erosion of the plant bed. However, volatile losses of iodomethane (more than 82% in the first 10 days) moving through the tarp and out the sides of the plant bed will be significant and were simulated by the 5 day half-life in the top one meter of the soil profile.

The resulting concentrations in the soil pore water at a one meter depth are presented in Table 1. The values simulated, ranging from 0 to 520 ppb for the 1 meter depth, are in the same range as values measured in the field dissipation study of 2, 26, 36, 76, 65, 102, 59, 209, 7, 0, and 0 for the 0, 0.3, 1, 2, 3, 5, 7, 14, 29, 59, and 90 days after application respectively for the soil iodomethane (EPA MRID No. 45593711). In the field dissipation study, there was no residual iodomethane in the 1.2 meter profile, 90 days after application.

The simulated concentrations at the 5 meter depth are significantly less than those at one meter. The maximum average iodomethane in the pore water is less than 2 ppb in both application months, however, the September surface meter concentrations are significantly larger than those of January (mean 40.98 vs 4.45 ppb). The average rainfall in September over the 30 year simulation period was more than 2 inches higher than February. The best correlation between iodomethane at the 1 meter depth and rainfall was with the sum of the 15 days following the application (R^2 = 0.62). The values in Table 1 are soil pore concentrations and are not free water to be consumed. The 5 meter depth (16 foot depth) is about the shallowest ground water that could reasonably be consumed. However, these concentrations are directly beneath the application area. Drinking water wells would probably be some lateral distance away from application areas since a buffer width of 25 to 500 feet from occupied dwellings is required. The PLUS (PRZM 3 Leaching-United States) model dilutes the pore water volume by 75% when shallow aquifer parameters common for Florida are used. This would provide drinking water values of less than 0.5 ppb for a maximum, and a mean of less than 0.05 ppb. Most applications of iodomethane in Florida will keep the tarp in place after application. These simulations probably actually overestimate the amount of leachate available for iodomethane. The tarp is impermeable to rainfall, decreasing the amount of water in the raised plant bed that can infiltrate the soil. Also, proper sub irrigation (drip) beneath the tarp should not provide excess moisture for downward movement of soluble chemicals.

Table 1. 30 year PRZM 3.12 simulations of pore water concentrations of iodomethane (ppb) at the 1 meter and 5 meter soil depths.						
Year	**1 Meter**		**5 Meters**		**Rainfall**	
	Jan.	**Sept.**	**Jan.**	**Sept.**	**Feb.**	**Sept**
	ppb				**Inches**	
1961	0.03	0.00	0.00	0.00	1.1	3.0
1962	0.16	2.11	0.00	0.00	3.0	9.0
1963	0.68	227.60	0.00	0.00	7.7	10.4
1964	62.53	21.26	0.02	0.00	11.1	11.7
1965	0.65	0.25	1.72	0.06	10.5	3.8
1966	9.73	43.06	1.31	1.00	17.5	10.0
1967	1.02	1.68	0.46	0.23	7.7	6.9
1968	0.70	54.94	0.22	0.03	10.9	11.9
1969	0.47	87.23	0.09	0.31	4.2	14.6
1970	7.09	0.19	0.05	0.14	7.6	7.6
1971	0.00	5.51	0.01	0.30	2.8	6.2
1972	0.07	0.18	0.11	0.40	6.5	3.7
1973	0.00	60.14	0.01	0.16	6.9	7.6
1974	0.00	0.19	0.00	0.01	1.1	5.6
1975	0.00	35.43	0.00	0.01	1.7	11.6
1976	2.40	1.45	0.00	0.01	11.4	7.7
1977	0.00	131.40	0.02	0.05	2.8	13.2
1978	0.02	1.89	0.06	0.04	6.3	6.4
1979	0.00	519.90	0.00	0.04	2.0	19.6
1980	8.03	0.63	0.00	0.44	9.8	7.0
1981	0.89	16.72	0.01	0.19	10.7	9.3
1982	2.22	1.96	0.20	1.66	5.9	6.0
1983	28.02	1.46	0.17	0.41	22.1	9.6
1984	8.35	0.60	1.92	0.09	11.4	9.9
1985	0.00	2.46	0.82	0.03	1.3	9.4
1986	0.00	0.03	0.19	0.01	4.0	4.1
1987	0.18	7.18	0.00	0.00	3.1	11.9
1988	0.11	0.00	0.00	0.01	7.7	2.0
1989	0.01	0.03	0.01	0.00	2.5	4.1
1990	0.00	4.03	0.00	0.00	3.5	11.7
Mean	4.45	40.98	0.025	0.19	6.8	8.5
Std. Dev.	12.31	102.90	0.51	0.35	5.0	3.9
Maximum	62.5	519.90	1.92	1.67	22.1	19.6

VIF Simulations for Ground Water

Since the VIF tarpaulin is 2.5 to 5 times less permeable for iodomethane than the HDPE tarp and allows more of the active ingredient to remain in the soil longer, concerns about leaching to shallow ground water needed to be addressed.

Tier II computer simulations with PRZM 3.12 (Plant Root Zone Model) in the USEPA, Express Shell v 1.00.00.03. were also used as had been done for the HDPE tarp. A biphasic approach was used to simulate soil volatilization losses with the VIF tarp before and after the tarp had been punctured. The Dover, FL EUP volatilization soil loss (Direct Method) data was used to simulate volatilization with the VIF tarp. This half-life (41 days) was used as the aerobic soil half-life for the top one meter of soil for the 21 days after the application while all other dissipation routes were set to zero (hydrolysis, volatilization, plant uptake). Once the tarp was punctured on DAY 21 a half-life of 13 days was used for the aerobic soil half-life in the upper one meter of the soil profile. It was assumed from the field dissipation data in the Plant City, FL study that there would be no iodomethane left in the top meter of soil 60 days after application. The punctured VIF tarp was assumed to be as permeable as the unpunctured HDPE tarp. In the soil profile below one meter (1 to 5 meters), the only dissipation route other than leaching was hydrolysis. The hydrolysis rate was set at a 100 day half-life. All other parameters used in the simulation were the same as those used in the HDPE simulations discussed above. The application rate was 87.5 lbs per treated acre and the entire acreage was treated.

Simulation results for soil treatments in January and September are presented in following tables. The concentrations in the soil from the 1 to 5 meter depth are the pore water concentrations before dilution occurs with aquifer water. The column labeled, "aquifer water" represents actual concentrations that could be consumed.

Table 6. 30-Year PRZM simulation of iodomethane in pore and ground water ((ppb) resulting from January treatments of a Florida topsoil						
Year	Pore Water					Aquifer Water
	1 m	2 m	3 m	4 m	5 m	5m
	ppb					
1961	9.0	0.2	0.0	0.0	0.0	0.0
1962	31.2	8.7	0.2	0.0	0.0	0.0
1963	9.7	3.6	1.0	0.2	0.0	0.0
1964	135.0	45.9	15.2	1.2	0.1	0.0
1965	5.8	1.1	5.8	5.1	0.8	0.2
1966	108.0	42.1	12.6	0.6	0.5	0.1
1967	18.7	4.4	6.3	4.5	0.7	0.1
1968	31.3	18.0	5.4	0.6	0.4	0.1
1969	31.7	14.3	7.0	1.8	0.8	0.2
1970	355.0	70.1	3.7	2.9	0.5	0.1
1971	3.6	9.2	7.8	0.6	0.2	0.0
1972	109.0	54.8	2.9	1.4	0.6	0.1
1973	6.0	3.9	5.8	1.5	0.1	0.0
1974	5.0	1.5	0.4	0.6	0.3	0.1
1975	6.9	0.9	0.2	0.0	0.0	0.0
1976	113.0	27.7	0.8	0.0	0.0	0.0
1977	13.4	6.6	4.2	1.1	0.1	0.0
1978	6.1	1.7	1.0	0.5	0.3	0.1
1979	10.5	3.6	0.4	0.1	0.1	0.0
1980	195.0	51.9	2.5	0.2	0.0	0.0
1981	19.8	6.1	8.9	1.2	0.1	0.0
1982	259.0	131.0	27.9	1.6	0.5	0.1
1983	337.0	109.0	39.0	15.4	5.3	1.1
1984	169.0	58.6	24.3	14.5	3.3	0.7
1985	9.2	3.0	9.6	3.1	1.6	0.3
1986	6.1	2.6	0.5	0.7	0.5	0.1
1987	66.6	16.3	1.0	0.2	0.0	0.0
1988	42.9	18.4	4.4	1.1	0.1	0.0
1989	9.6	2.1	2.3	0.4	0.2	0.0
1990	9.5	2.2	0.3	0.2	0.1	0.0
Mean	71.1	24.0	6.7	2.0	0.6	0.1
Std Dev	99.5	33.2	9.1	3.7	1.1	0.2
Range	351.4	130.8	39.0	15.4	5.3	1.1
Min.	3.6	0.2	0.0	0.0	0.0	0.0
Max.	355.0	131.0	39.0	15.4	5.3	1.1

Table 7. 30-Year PRZM simulation of iodomethane in pore and ground water ((ppb) resulting from September treatments of a Florida topsoil						
Year	←———— Pore Water ————→					Aquifer Water
	1 m	2 m	3 m	4 m	5 m	5m
	———————— ppb ————————					
1961	0.1	0.0	0.0	0.0	0.0	0.0
1962	89.1	0.0	0.0	0.0	0.0	0.0
1963	68.5	6.0	0.0	0.0	0.0	0.0
1964	403.0	23.7	1.9	0.0	0.0	0.0
1965	56.5	63.0	5.1	0.3	0.0	0.0
1966	575.0	61.6	21.7	1.7	0.1	0.0
1967	57.1	112.0	17.1	5.3	0.4	0.1
1968	679.0	65.9	32.8	5.1	1.5	0.3
1969	651.0	207.0	24.2	12.6	1.9	0.4
1970	51.0	183.0	85.3	7.3	4.7	0.9
1971	63.2	90.7	26.1	9.9	1.8	0.4
1972	400.0	14.5	33.3	10.6	2.5	0.5
1973	86.2	57.8	3.3	7.8	2.5	0.5
1974	58.2	40.9	8.5	1.7	1.8	0.4
1975	50.3	16.5	11.3	1.0	0.7	0.1
1976	137.0	9.2	4.3	2.4	0.2	0.0
1977	121.0	22.5	2.1	1.1	0.4	0.1
1978	133.0	26.2	4.8	0.6	0.3	0.1
1979	99.5	28.7	5.8	0.9	0.1	0.0
1980	136.0	28.8	8.4	1.7	0.2	0.0
1981	46.7	26.6	5.6	1.7	0.3	0.1
1982	471.0	23.3	7.5	1.7	0.5	0.1
1983	231.0	146.0	13.2	2.7	0.7	0.1
1984	204.0	70.8	50.9	5.0	0.9	0.2
1985	36.2	42.4	14.4	11.8	0.8	0.2
1986	122.0	27.4	13.1	5.1	2.1	0.4
1987	124.0	20.4	8.1	3.6	1.6	0.3
1988	186.0	37.1	4.8	2.3	1.0	0.2
1989	10.8	21.9	6.8	0.8	0.5	0.1
1990	107.0	18.5	4.0	0.8	0.2	0.0
Mean	181.8	49.7	14.1	3.5	0.9	0.2
Std Dev	191.3	51.4	17.9	3.7	1.1	0.2
Range	678.9	207.0	85.3	12.6	4.7	0.9
Min.	0.1	0.0	0.0	0.0	0.0	0.0
Max.	679.0	207.0	85.3	12.6	4.7	0.9

Only in the shallowest ground water (< 2 meters) are the iodomethane concentrations above 50 ppb. Even with the VIF tarp holding more of the iodomethane in the soil for a greater time than the HDPE tarp, there are still few concerns with potable ground water being degraded by iodomethane enrichment. The predicted groundwater concentrations were compared to the groundwater guidance concentration of 520 ppb that Arysta LifeScience calculated. This calculation was based on the outcome of the dog 90-day, oral exposure study which identified a NOAEL value of 1.5 mg/kg.

Environmental Fate Studies for Iodomethane

Hydrolysis

The hydrolysis of ^{14}C-iodomethane was studied in the dark in buffered solutions at pH 4, 7 and 9. Samples were incubated in the dark at 25°C for up to 30 days. Volatiles were not trapped. The behavior of iodomethane was independent of pH. Methanol was the only transformation product and was 16 to 18% of the applied radioactivity (AR). Other degradates (unidentified) totaled less than 1.85% AR. The half-lives for iodomethane were 105, 94, and 108 days for pH 4, 7 and 9 respectively. Iodomethane reacts with water to form methanol and iodide.

Aqueous Photolysis

In the aqueous photolysis study, 11 mg ^{14}C-iodomethane were dosed into a pH 5 buffer and irradiated continuously with light from a xenon arc lamp for up to 15 days. Volatiles were not trapped. In the irradiated samples 14C-iodomethane decrease form 99.33% on DAY 0 to 44.9%AR on DAY 15. The major transformation products were formaldehyde and methanol which reached maximums of 36.5 and 18.7% of the AR by DAY 15. There were no minor transformation products.

The proposed pathway of degradation is iodomethane hydrolyzed to iodine radicals and methanol which is eventually oxidized to formaldehyde.

The dark control decreased from 99.3% to 88-90.5% of the AR by DAY 15. The major transformation product in the dark incubation was methanol at 10.5% AR. The half-lives of iodomethane in the continuous irradiation and dark treatments were 13 and 83.5 days respectively. The aqueous photolysis half-life for iodomethane for continues irradiation corrected for the hydrolysis in the dark is 15.3 days or 30.6 days fro a 12 hour light-dark cycle. This light intensity is equal to that of Ohio in early summer.

Aerobic Soil Metabolism

The aerobic soil metabolism was determined on a sandy loam topsoil (California) with 1.48% organic matter and a pH of 6.5. Topsoil samples were dosed with the equivalent of 35Kg/ha and incubated in the dark at 20°C for up to 288 hours (12 days). The test systems consisted of sealed test columns with soil and a continuous flow through to collect CO_2 and other volatiles.

Iodomethane rapidly dissipated from the soil decreasing from 95% of the applied radioactivity (AR) at time 0 to 43 to 56% AR (Hour 2) and1% AR by Hour 24. No major transformation products were detected in the soil. Volatilization of ^{14}C-iodomethane was 95% of the AR. CO_2 and other volatiles were 1.1 and 2.6% AR respectively.

The half-life of iodomethane in the soil was 2.1 hours based on first order linear regression. This half-life is almost totally due to volatilization.

Anaerobic Aquatic Metabolism

The anaerobic soil metabolism study was conducted on a sandy clay loam sediment with an organic matter content of 2.08% and a pH of 8.0. The soil samples were pre-incubated in water (1:3 soil: water) for 22 days to establish anaerobic conditions. The water had a pH of 8 and a dissolved organic carbon of 6.93 mg/L. After the pre-incubation, the sediment/water systems were dosed with 13 mg/L of ^{14}C-iodomethane and incubated in the dark at 20°C for up to 14 days.

^{14}C-iodomethane decreased from 94 to 99% AR on TIME 0 to 51% (DAY1), 23% (DAY3), to 1.1% AR (DAY 14). ^{14}C-iodomethane was detected mainly in the water layer and decreased from a high of 85 to 89% AR to <1% AR (DAY 14). Iodomethane decreased in the sediment form 8 to 10%AR at Hours 0 to 4, to 1.4 to 2.3% at DAYs 3-4. No major transformation products were detected in the water or sediment layers. One minor product methanol, reached 4.8% AR in the water column.

^{14}C-iodomethane volatilized from the water-sediment systems from 15% (Hour 4), 50% (Day 4) to 55-60% AR (DAY 14). At DAY 14 CO_2 and unidentified volatiles accounted for 5.2 to 6.7% AR. The first order regression of the iodomethane half-lives for the total system, water layer and sediment layer are 40, 39, and 38 hours respectively. Iodomethane dissipated from the anaerobic water-sediment systems via volatilization with minor accumulations of applied radioactivity as methanol, CO_2, unidentified organics, and sediment residues.

Soil Adsorption/Desorption

In a batch equilibrium study the adsorption of iodomethane labeled with ^{14}C was completed on five soils representing a wide range of textures and organic matter contents. The Kd values ranged from 0.4 to 1.2 ml/g. The corresponding Koc values ranged from 14 to 61 mL/g. Iodomethane has a low affinity for adsorption to soil particles and should readily move with water.

Terrestrial Field Dissipation Studies

Field dissipation studies on bare ground were conducted in California and Florida. The California soil had a loam texture throughout the profile with 30 to 44% sand, and 18 to 22% clay. The Florida soil had 90 to 88% sand throughout the profile (1.8 m depth) with the HDPE tarp.

Pesticide applications were by shallow shank injection (20 cm depth) immediately followed by tarping of the raised bed. At the Florida site soil samples were taken on 0, 0.3, 1, 2, 3, 5, 7, 14, 29, 59, and 90 days after the application to a depth of 122 cm at approximately 15 cm increments. The Florida site received 258.8 lbs/acre of iodomethane to raised beds with HDPE tarping. Only 50% of the site was fumigated which reduced the application rate to 129 lbs/acre.

<u>Florida:</u> Iodomethane was distributed throughout the 122 cm deep soil profile, decreasing with depth. Iodomethane decreased from the maximum of 12.29 mg/kg soil in the 0-15 cm soil sample on DAY 0 to 1.168 mg/kg on DAY 5 for the 0-15 cm depth sample. Iodomethane was not detected at DAY 90 in the soil profile and on DAY 59 was only 0.001 mg/kg (0-15 cm), 0.008 (30-45 cm) and 0.002 (91-107 cm). At the bottom of the soil profile (107-122 cm) the peak iodomethane concentrations were on DAY 14 at 0.209 mg/kg but decreasing to 0.007 and 0.000 on DAY 29 and 59 respectively. Iodomethane was detected in the buried soil sample (152-183 cm) with a peak of 0.029 mg/kg (DAY 2) and 0.022mg/kg (DAY 8).

The estimated field dissipation half-life is 5.0 days. A total of 82.4% of the applied iodomethane volatilized from the soil in the first 10 days. At the end of the 90 day trial there were no soil profile residues for carryover. The disappearance of iodomethane or iodide from the profile due to leaching does not appear to be a significant pathway with respect to water quality.

Iodide:

The rapid volatilization of iodomethane from the soil limits the iodide concentration. Iodide anions form as iodomethane is demethylated upon contact with soil organics. Iodide can air-oxide to iodine which can be lost by volatilization to the atmosphere. Iodide was measured in the soil profile on DAY 7, 14, and 29. Peak concentrations on DAY 14 were 1.70 mg/kg at the 0-15 cm depth but decreased to peaks of 0.11 mg/kg at the 30 to 45 cm depth. Iodide was less than 0.01 at the 107-122 cm depths. Decreases in the iodide content in soil were not due to leaching since it did not appear in the lower soil profile. The soil background in the control plots was less than 0.01 ppm iodide throughout the soil profile.

<u>California:</u> At the California site, the field dissipation half-life was estimated at 4.8 days. The deepest Iodomethane measured was 1 ng/kg on DAY 15 at the 122 to 137 cm depth. By DAY 28 the deepest residues were 1 ng/kg at the 61 to 76 cm depth. The highest concentrations were either in the 0-15 cm samples (7.04 to 2.2 mg/kg) or the 15 to 30 cm depth (3.8 to 1.3) during the first 4 days.

After DAY 4 the maximum soil concentrations were 0.37mg/kg (15 to 45 cm) on DAY 8, 0.048 mg/kg (15-30 cm) DAY 15, .017 mg/kg (30-45 cm) DAY 28 and 0.002 mg/kg (15-30 cm) DAY 57. Iodide concentrations were measured on DAY 8, 15, and 28. The peak concentration was 2.32 mg/kg (0-15cm) on DAY 15. Iodide below the 61 cm depth ranged from 0.01 to 0.02 mg/kg to a depth of 183 cm in the soil.

Volatilization was the major route of dissipation in the two field trials. After 9 days of treatment 58.4% and 82.4% of the iodomethane was lost from the soil in the California and Florida sites respectively.

Offsite Air Dissipation Studies

The offsite air movement of iodomethane was studied at the California site with a broadcast injection into the soil. The application rate was 235 lbs/acre. Twelve sampling stations were located at 30 feet outside the treatment area. Four sampling stations were 141 feet diagonally from the corners of the treatment site. Air sampling stations had a personal air sampling pump attached to masts at 5 feet above the ground. Air samples were collected on the treatment day at hours 1 to 2, 2 to 4.5, 4.5 to 8 and 8 to 18. On DAY 1 to 10 after the treatment samples were taken at 12 hour increments.

Iodomethane ranged from less than the limit of detection (LOD) to 2,566ug/m^3. In the first 12 hours the flux rate averaged 115ug/m^2-s. The second 12 hour sampling (hour 12 to 24) had a flux rate of 17ug/m^2-s. Flux rates decreased from 481, to 276, to 87 to 48ug m^2 s for the 0 to 3, 3 to 6, 6 to 8, and 8 to 19 hour periods respectively. In the 12 hour sampling after the first day the maximum in air was 190 ppbv on DAY 3 which decreased to 20 by DAY 10. A diurnal component was observed with the daylight flux rate greater than the night.

The mean ambient iodomethane air concentration in urban areas in a 1972 to 1985 study was reported as 0.02 ppbV (parts per billion volume basis). Another study reported a mean of 0.04 ppbv with a maximum of 0.08. The air concentration over the ocean is 0.5 to 1.0 ppbV. Half-lives of iodomethane in air above the Florida and California soil dissipation studies as regressed with a first order equation ranged from 1 to 2.8 days with means of 1.3 and 2.0 days respectively. Iodomethane in the atmosphere photolyzes rapidly to iodine and methyl radicals. The methyl radicals can react with atmospheric moisture to form methane or methanol. The literature suggests a half-life of iodomethane in the troposphere of around 4 days.

<u>On-Site Dissipation</u>:
In Manteca, California iodomethane was broadcast shank applied at a rate of 242 lb/acre and covered with 1 mil plastic tarp. Volatilized iodomethane was collected in the field center at 15, 30-, 50, 80 and 150 cm above the ground. The volatilization rate was 481, 276, 87, and 48ug/m^2-sec for hours 0 to 3, 3 to 6, 6 to 8 and 8 to 19 following treatment of DAY 0. Volatilization on DAY 1 (0 to 12 hrs) increased to 115 before decreasing to 17ug/m^2-sec for hours 12 to 24. Volatilization ranged from 6 to 34ug/m^2-sec on DAY 2, 3 to 32 on DAY 3 through 8 and 3 on DAY 9 and 10. A diurnal fluctuation with greater daytime flux than night was observed. In the 10 days before the tarp was removed, 94% of the applied iodomethane was lost from the soil. The greatest mass of iodomethane lost was on hours 0 to 3 (21%). In the 24 and 48 hours following application 41 and 62% of the applied iodomethane was lost from the soil. Average concentration of iodomethane at a 30 cm height on DAY 1, 2, 4, 7 and 10 were 2013, 428, 700, 363, and 71ug/m^3 respectively. Using the equation: ppbv = (ug/m^3 (24.45)/ (142), the concentrations above corresponds to 346, 74, 120, 63, and 12 ppb on a volume basis.

Volatilization in Experimental Use Studies.

In Florida an EUP study determined the volatilization of iodomethane and chlorpicrin by both the direct and indirect method. Midas 50:50 (181 lbs) was applied to raised beds in a 2.5 acre plot. The beds were covered with VIF (Virtually Impermeable Film) tarpaulin. The VIF is tarpaulin with metallized, white plastic. The fumigated area was 1.25 acres of the plot. The application rate for iodomethane was 36.2 lbs/acre or 72.4 lbs per treated acre. Air samples were taken continuously for 7 days after the application in field and around the perimeter at 0 to 12 and 12 to 24 hour intervals. Air sample tubes in the center of the field were used for the direct flux determination and were attached to masts at 15, 33, 55, 90 and 155 cm above the soil surface. The perimeter air sampling tubes were used for the indirect flux determination and were attached to masts at 1.5 meters above the soil surface. The trapping efficiency and transport stability of iodomethane was estimated to be 86%. The 2.5 acre application took 3.5 hours.

Direct flux measurements estimated that 12.1% of the iodomethane was lost from the soil during the first 7 days after application (Table 6). The first 24 hours after application had a flux loss of 4.2% of the applied iodomethane. Indirect flux measurements were 9.2 and 25.5% for the 24 hour and 7 days respectively.

Table 6. Comparison of Volatilization between the Direct and Indirect Methods and between HDPE and VIF tarps.

Site	Direct Method			Indirect Method		
	24 hrs	7 Days	10 Days	24 hrs	7 Days	10 Days
	----------- % Volatilization From Soil -------------					
Plant City (HDPE)	---	---	---	48	71	82
Dover (VIF)	4.2*	12.1*	15†*	9.2	25.5	---

† *Extrapolated from volatilization curve as an additional 1%/day*
* *Unadjusted for trapping efficiency of 0.86.*

Flux rates in the Plant City study were estimated by the indirect method as 48, 71, and 82% for the 24 hour, 7 and 10 days respectively (Table 5). The Indirect Method, with off field trapping appears to over estimate volatilization from soil 2-fold when compared to the Direct Method with trapping within the field. Therefore the direct method of volatilization should be around 24% and 35% for the 24 hour and 7 Days respectively at the Plant City Site.

The lower emission in the EUP studies as compared to previous studies was due to the VIF film being more impermeable to iodomethane than the HDPE (high density polyethylene), and the "Symmetry" application equipment. The VIF and "Symmetry" equipment appear to be about 5 times more effective in keeping the iodomethane in the soil over the first 24 hours after the application. By DAY 7 and 10 the HDPE allow 2.5 and 2.3 times more iodomethane out of the soil. The larger differences in the efficiency trapping on DAY 1 when compared to DAY 7 may reflect the reduction in volatilization losses due to the application equipment. The amount of iodomethane applied (258.8 lb/acre (HDPE) vs 72.4 lb/treated acre (VIF) and rainfall during the 2nd day may have also attributed to the lower volatilization experienced with VIF in the EUP study.

The in-field masts had time weighted average peaks of 20 to 50 ppb during the first 10 hours after application. In-field concentrations were less than 10 ppb after 30 hours. The highest concentrations were in the 15 cm height samples. The perimeter masts (1.5 meter height) that were 60 feet away from the field edge had time weighted average peaks of 4 to 13 ppb within the first 10 hours after application and decreased to less than 2 ppb after 40 hours. Offsite sampling tubes in the downwind direction had higher concentrations of iodomethane. Concentrations were generally consistent with wind speed/direction and temperature.